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(54) Title of the Invention: **ELECTRON BEAM-CURABLE ADHESIVE FOR LAMINATE**

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## SPECIFICATION

### 1. Title of the Invention

ELECTRON BEAM-CURABLE ADHESIVE FOR LAMINATE

### 2. Claims

An electron beam-curable adhesive for laminates, characterized in that it comprises 10 to 95 weight parts acrylic monomer represented by the following structural formula:

$$CH_2{=}CHCOOR^1OCONHR^2$$

(where $R^1$ is a $C_2$ to $C_4$ alkylene, and $R^2$ is a $C_1$ to $C_{18}$ alkyl, phenyl, or cyclohexyl) and 5 to 40 weight parts of one or more of polyurethane resins, polyester resins, polyvinyl acetate resins, and acrylic resins, which have a molecular weight of between 5,000 and 500,000.

## 3. Detailed Description of the Invention

The present invention relates to improvements in a laminate adhesive for plastic films, and in particular to an adhesive which can be rapidly cured by an electron beam to provide a flexible adhesive layer with high adhesive strength.

Dry lamination, extrusion lamination, and wet lamination are examples of methods for producing laminate films of widely used plastics, including packaging materials. All involve the use of adhesives, most often adhesives such as polyurethane, polyacrylate ester, epoxy, vinyl chloride-vinyl acetate copolymer, and isocyanate adhesives or the like.

However, since all of these adhesives are used while dissolved in organic solvents such as ethyl acetate, methyl ethyl ketone, toluene, xylene, and hexane, the organic solvent can be volatilized during adhesion or while drying, not only adversely affecting the working environment, but also making it necessary to employ heating for drying purposes, which is costly, and even dangerous. The use of large amounts of organic solvents can cause air pollution and does not represent a desirable use of resources. Because organic solvents are left over, if only in minute amounts, in laminate film products, such laminates are inappropriate for packaged products such as food, which will take on the odor of the solvent.

In addition to the aforementioned general problems, a particular drawback is that adhesion takes some time in plastic film laminates with high barrier properties. That is because this type of laminate is preferably obtained by dry lamination in order to ensure high adhesive strength, normally involving the use of a mixture of resins affording initial adhesive properties with a combination of liquid polyols and polyisocyanates as the adhesive. Because such adhesives are cured as a result of increased molecular weight and crosslinking upon the formation of urethane bonds through reaction between the hydroxy groups of the polyol and the isocyanate groups of the polyisocyanate, there is no adhesive strength immediately after lamination. It is not until the laminate has been set aside for 5 to 7 days for the reaction to be completed that the process can move to the next step. It thus cannot be determined whether the desired lamination has been achieved until after that time has passed, which is a disadvantage when it comes to quality control.

The present invention is intended to overcome the drawbacks described above through the use of an electron beam-curable adhesive. Electron beam-curable adhesives are solvent-free, thus completely bypassing any problems associated with the use of solvents, and are also cured more rapidly, thus ensuring higher productivity. The recent availability of relatively smaller electron beam radiation devices that are not very expensive has proved to be advantageous in that the equipment is less limited, with no need for large furnaces to dry solvent-based adhesives. Because such devices can also be turned on and off instantaneously, the process is easier to control, while another advantage is that less material is lost. As such, electron beam curing has been widely used, primarily in the manufacture of laminate films for packaging materials.

However, known electron beam-curable adhesives result in cured layers with poor flexibility, and do not provide satisfactory adhesive strength.

An object of the present invention is to overcome the above drawbacks by providing a laminate adhesive with both high adhesive strength and good cured layer flexibility, while preserving the advantages of electron beam-curable adhesives, namely, the fact that they are solvent-free and rapidly cured. That is, the present invention is, in essence, an electron beam-curable adhesive for laminates, characterized by comprising 10 to 95 weight parts acrylic monomer represented by the following structural formula:

$$CH_2{=}CHCOOR^1OCONHR^2$$

(where $R^1$ is a $C_2$ to $C_4$ alkylene, and $R^2$ is a $C_1$ to $C_{18}$ alkyl, phenyl, or cyclohexyl)

and 5 to 40 weight parts of one or more of polyurethane resins, polyester resins, polyvinyl acetate resins, and acrylic resins, which have a molecular weight of between 5,000 and 500,000.

Acrylic monomers $CH_2=CHCOOR^1OCONHR^2$ (where $R^1$ is a $C_2$ to $C_4$ alkylene, and $R^2$ is a $C_1$ to $C_{18}$ alkyl, phenyl, or cyclohexyl) can be obtained by a reaction between, for example, an isocyanate alkyl ester, isocyanate cyclohexyl ester, or isocyanate phenyl ester and hydroxymethyl acrylate, hydroxypropyl acrylate, or hydroxybutyl acrylate. The aforementioned acrylic monomer should be used in an amount of 10 to 95 weight parts. Less than 10 weight parts will result in poor adhesive strength, while more than 95 weight parts will result in unsatisfactory cohesion.

The second component is a polyurethane resin, polyester resin, polyvinyl acetate resin, and/or acrylic resin, with a molecular weight of between 5,000 and 500,000, which is included in order to modify the viscosity of the adhesive and improve the adhesion on plastic films. It should be used in an amount of 5 to 40 weight parts. Less than 5 weight parts will not produce the intended effects, while more than 40 weight parts will not result in any further improvement in adhesion.

Polyurethane resins which can be used for the aforementioned purpose include those polyurethane resins obtained by a reaction between a polyether type polyol and a diisocyanate, which are miscible with the acrylic monomer serving as a primary ingredient of the adhesive. Examples of commercially available products include Desmocoll 110, 130, 400, 406, 420, and 510 granular polyurethane resins (produced by Sumitomo Bayer Urethane), and Nippolan (produced by Nippon Polyurethane Industry Co., Ltd.).

Polyester resins should be those polyester resins obtained by melt polymerization of a diol and a dicarboxylate ester, or direct polymerization of a diol and a dicarboxylic acid, which are miscible with the above acrylic monomer. Ideal commercially available products include linear polyester resins such as Vylon (from Toyobo Co., Ltd.) and Vitel (from Goodyear).

Vinyl acetate resins should be vinyl acetate homopolymers or copolymers comprising at least 5 mol%, and preferably at least 30 mol% of such a homopolymer, that are miscible with the acrylic monomer. Examples of commercially available products include Esuniru and Esurekku (from Sekisui Chemical Co., Ltd.), Goseniru (from Nippon Gosei), and Bakelite (from Union Carbide).

Acrylic resins include acrylate ester- or methacrylate ester-based polymers which are soluble in the above monomer. Examples of commercially available products include Acrybase (from Fujikura Kasei) and Paraloid (from Rohm and Haas).

The electron beam-curable adhesive for laminates in the present invention can also contain an acrylate ester monomer to modify the curing rate and improve miscibility between the various components. Examples of acrylate monomers include methyl acrylate, ethyl acrylate, n{iso}-butyl acrylate, 2-ethylhexyl acrylate, isodecyl acrylate, lauryl acrylate, stearyl acrylate,

ethylene glycol diacrylate, di{tri}ethylene glycol diacrylate, (di)propylene glycol diacrylate, neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, methyl triglycol acrylate, 1,5-pentanediol diacrylate,

trimethylolpropane triacrylate, methoxyethyl acrylate, n-butoxyethyl acrylate, ethylcarbitol acrylate,

dipentaerythritol hexacrylate,

diethylaminoethyl acrylate,

benzyl acrylate,

tetrahydrofurfuryl acrylate,

2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, acryloyloxyethyl monosuccinate, and acryloyloxyethyl monophthalate. The acrylate ester monomer should be added in an amount of no more than 80 weight parts, and preferably no more than 40 weight parts. More than 80 weight parts will result in a lower concentration of urethane bonds in the adhesive, leading to lower adhesive strength.

To improve the storage properties of the adhesive, a polymerization inhibitor such as a hydroquinone or a catechol should be added in the necessary amount, usually about 0.001 to 0.5%. A plasticizer or extender pigment can also be added as needed to the adhesive.

Primary applications for the adhesive of the present invention are homogenous or heterogeneous plastic films, but the adhesive is also useful for paper, metal foil, or laminates of these with plastic film. It can be used in an extremely wide range of plastic films, examples of which include cellophane, copolymers of low density-, medium density-, and high density-polyethylene, polypropylene, or ethylene and other α-olefins, ethylene-vinyl acetate copolymers, ethylene-vinyl alcohol copolymers, poly-1,2-butadiene, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol, polyethylene terephthalate, polyamides, polycarbonates, polyacetates, ionomer resins and similar drawn or undrawn films, as well as such plastic products coated with polyvinylidene chloride, or metal deposited films such as aluminum. A corona discharge treatment or the like may be performed before the adhesive is applied in order to ensure better adhesive strength.

To produce a film laminate using the adhesive of the present invention, the method should include a step in which the adhesive is applied, in a proportion of 0.2 to 20 g/m$^2$, and preferably 0.4 to 10 g/m$^2$, by a method such as gravure coating, roll coating, or flexo reverse printing on all or part of a base film surface, another film (either the same as or different from the base film) is placed on top or another material is extruded onto the film, and the adhesive is then cured by electron beam radiation.

To make a laminate of 3 or more layers, the double-layered laminate film obtained in the manner described above can be used as the base, and the method described above can be repeated, or 3 or more films can be placed on top of each other with the adhesive of the invention applied between each layer, and the adhesive between the layers can be cured all at once by a single dose of electron beam radiation.

The electron beam for curing the adhesive is advantageously discharged from any of various electron beam accelerators, with an energy of 50 to 1000 KeV, and preferably 100 to 300 KeV. The adhesive layer may be irradiated by either spot beam high-speed scanning or a curtain beam. Usually, the material being irradiated is continuously moved to allow the surface to be irradiated.

The invention can thus be worked in an industrially useful manner to produce a laminate film using a solvent-free adhesive. The final laminate film product will be extremely useful as packaging material, particularly for packaging various types of food products, drug products, and the like.

Example 1

As a mixture of 205 weight parts 2-hydroxyethyl acrylate and 0.1 weight part dibutyltin dilaurate was stirred, 100 weight parts of methyl isocyanate was added in the form of drops. The reaction was brought about as the reaction temperature was controlled to no more than 60°C, giving methylcarbamoyloxyethyl acrylate ($CH_2=CHCOOC_2H_4OCONHCH_{\text{[illegible]}}$). 10 weight parts polyurethane resin (Desmocoll 130, from Sumitomo Bayer urethane) was dissolved in 90 weight parts of the resulting methylcarbamoyloxyethyl acrylate, giving an adhesive composition.

The adhesive was applied in a proportion of 2.5 $g/m^2$ by off-set gravure printing to biaxially oriented polyethylene terephthalate film (Lumirror, from Toray; 16 μ thick), and a 40 μ thick polyethylene film was placed on top.

As this laminated film was taken up at a rate of 30 m/min, it was irradiated with 3 Mrad radiation under conditions involving 150 KeV and 15 mA using an electron beam radiation device (Electrocurtain, from ESI of the United States) to cure the adhesive.

The adhesive strength of the resulting laminate film was determined with a Tensilon at a pulling speed of 50 mm/min and a separation angle of 90° (T-shaped). The adhesive strength was in the range of 430 g/15 mm or more, and the film tore when attempts were made to separate the layers.

Examples 2 - 4

The following table summarizes the results obtained for similarly obtained laminates.

The following abbreviations are used in the table.

ON (16): oriented nylon (16 μ thick)

CPP (60): undrawn polypropylene (60 μ thick)

PET (12): oriented polyethylene terephthalate (12 μ thick)

PE (40): undrawn polyethylene (40 μ thick)

OPP (20): oriented polypropylene (20 μ thick)

| Examples | Acrylic monomer | | | added monomer (weight parts) | resin (weight parts) | laminate structure | adhesive strength (g/15 mm) |
|---|---|---|---|---|---|---|---|
| | hydroxyalkyl acrylate | isocyanate ester | reaction product (weight parts) | | | | |
| 2 | 2-hydroxyethyl acrylate | butyl isocyanate | butyl carbamoyloxy | 2-hydroxy-3-phenoxy | Esuniru C-2 (vinyl | ON (16)/CPP | 680 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | ethyl acrylate (40) | propyl acrylate (30) | acetate resin from Sekisui Chemical) (30) | (60) | |
| 3 | 2-hydroxypropyl acrylate | phenyl isocyanate | phenyl carbamoyloxy ethyl acrylate (10) | 2-hydroxy ethyl acrylate (70) | Vylon 560 (polyester resin, from Toyobo) (20) | PET (12)/PE (40) | 540 |
| 4 | 2-hydroxyethyl acrylate | ethyl isocyanate | ethyl carbamoyloxy ethyl acrylate (70) | -- | ethyl polyacrylate (30) | OPP (20)/CPP (20) | 320 |